

# PATENT SPECIFICATION

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# PROVISIONAL SPECIFICATION

# Improvements in or relating to the Production of Cyanine Dyestuffs and to the Sensitising of Photographic Emulsions

We, ILFORD LIMITED, a British Company, of 23. Koden Street, Ilford, in the County of Essex, do hereby declare the nature of this invention to be as 5 follows:—

This invention relates to the production of cyanine dyestuffs and particularly to the production of symmetrical dicarbocyanine dyestuffs containing substituents 10 in the polymethine chara. It further relates to the sensitising of photographic emulsions.

According to the present invention cyanine agestuffs are prepared by condensing a corapound of the general formula I:—

$$\begin{array}{c|c} \text{OHG} & \\ x - \text{GH} & \text{G} - \text{R}_{\underline{1}} \\ \end{array}$$

where R, is a nitrile (CN) or carboxylic ester (COOR) group and X is a thioether 20 (—SR) or anil (NHR) group, R being a hydrocarbon group, with a heterocyclic nitrogen compound containing a reactive methylene group.

More particularly, according to this invention, the said heterocyclic compound 25 conforms to one or other of the following general formulæ II and III:—

$$R_{2} Y_{1} = (OH - OH)_{TL} = O - CH_{3}$$

where R<sub>2</sub> is an alkyl, hydroxyalkyl or 30 aralkyl group, Y<sub>1</sub> is an acid radicle, D<sub>1</sub> is the residue of a five-membered or six-membered heterocyclic ring, n is nought or one. R<sub>3</sub> is a hydrogen atom or an alkyl, aralkyl or aryl group and D<sub>2</sub> is the residue 35 of a heterocyclic nitrogen-keto-methylene nucleus.

Accordingly as compounds of fermulæ II or III are employed, at the products conform to formulæ IV or V:—

$$R_1$$
  $R_2$   $R_3$   $R_4$   $R_5$   $R_6$   $R_7$   $R_7$ 

The condensation may be effected in the presence of a base or in the presence of an acid anhydride together with a base. A base such as pyridine is suitable, but

it is preferred to use a stronger base such as triethylamine or sodium acetate in conjunction with a carboxylic acid anhydride such as acetic anhydride.

As already indicated R, may be a nitrile group or a carboxylic ester group. Examples of the latter are groups of the form -COOR where R is an alkyl, e.g. 5 methyl, ethyl, propyl, butyl or higher alkyl group, an aralkyl group, e.g. benzyl or naphthyimethyl, or an aryl group, e.g. phenyl or naphthyl. R2 may be any of the foregoing alkyl or aralkyl groups, or 10 may be a hydroxyalkyl group such as  $\beta$ hydroxy ethyl or \gamma-hydroxy propyl. Where R2 is an hydroxyalkyl group this will usually by acylated by the acid condensing agent so that R2 in the product 15 will be an acyloxyalkyl group. R3, if not a hydrogen atom, may be any of the foregoing alkyl, aralkyl or aryl groups.

Y, may be any acid radicle, for example halide (chioride, bromide, iodide), sulphate, sulphamate, perchlorate or p-

toluene sulphonate.

Di may be the residue of any five-menibered or six-membered heterocyclic ring system including thiazoles, oxazoles, selenazoles and their polycyclic homologues such as those of the benzene, naphthalene, acenaphthene and anthracene series; pyridine and its solveyelic homologues, such as quinoline and a and B-naphthoquino-30 lines; lepidines; indolenines; diazines such as pyrimidines and quinazolines; diazoles (e.g. thio-\$\beta\beta^1\-diazole); oxazolines, this solines and selenazolines. The polycyclic compounds of these series may 25 be substituted in the carbocyclic rings wiel, one or more groups such as alkyl, aryl, amino, hydroxy, alkoxy and methylene dioxy groups, or by halogen

D, may be the residue of rhodanic acid (2-thio - 4 - keto-teirshydrothiazole), oxarhadania acid (2-thio-4-keto-tetrahydrooxazole) and the N-aydrocarbon substitured derivatives of such compounds. 45 oxindoles, pyrazole-5-ones, hydantoin.

thio - hydantoin, pseudohydantoin and

pseudothiohydantoin.

The initial starting compounds of general formula I may be prepared by 50 reserves a compound of the formula CII, R. i.e. accionitrile or an acetic ester, with a formic enter (preferably ethyl formate) in the presence of powdered This yields the compound sedium. 55 R. - CH. - "HC as are sodium salt. This product is from reneved with a mercaptan REAL to the presence of ary hydrochloric acid, or is reacted with aniline to produce the thicefor or anil of the formula 60 R, - VH = CH-X. This latter compound

is reacted further with a formic ester (preferably ethyl formate) and powdered sodium to vield a product of the formula I as required for use in the present

65 invention.

Many of the dyestuffs formed according to this invention are sensitising dyes for silver halide photographic emulsions.

The following illustrate the preparation of compounds of general formula I:-

A. PREPARATION OF a-CARBETHONY MALON-DIALDEHYDE MONO ANIL.

10 parts of sodio formyl ethyl acetate were dissolved in 100 parts of water and added with stirring to a solution of 7 parts 75 of aniline in a mixture of 40 parts of acetic acid and 160 parts of water. The ethyl-anilinomethylene acetate was precipitated as a flocculent yellow solid. M.pt. 105°.

This preparation is analogous to that of v. Pechmann, Berichte der Deutschen Chemischen Gesellschaft, 25, 1047.

A suspension of 30 parts of the above ethyl-anilinomethylene acetate in 100 85 parts of dry ether and 11.7 parts of ethyl formate was added in portions to 3.62 parts of sodium powder under 200 parts of dry ether. A slight reaction ensued and afterwards the solution was refluxed 90 for 8 hours and then poured into water under an atmosphere of CO2. The water was ether extracted, the extracts dried over sodium sulphate and the ether removed by distillation. The product was 95 distilled under reduced pressure, b.pt. 197° at 8 mm. pressure to give an oil which solidified on cooling to a yellow crystalline mass.

B. PREPARATION OF ETHYL-a-FORMYL-B- 100 ETHYLITIO ACRYLATE.

14 parts of sodio formyl ethyl acetate and 25 parts of ethyl mercaptan were mixed together with 25 parts of dry ether, and dry HCl gas passed through 105 the mixture for 2 hours with cooling. After being allowed to stand overnight. the solution was poured into dilute sodium carbonate solution, ether extracted, dried over socium sulphate 110 anhydrous, and the ether evaporated. Distillation under reduced pressure yielded B-ethyithio ethyl acrylate. B.pt. 160-165° at 30 mm. pressure.

11 parts of the above  $\beta$ -ethylthioethyl 115 acrylate and 6 parts of ethyl formate were mixed with a little dry ether and reacted with 1.5 parts of sodium powder also under dry ether. After addition the mixture was heated for 24 hours and 120 poured into water under an atmosphere or earbon dioxide. The aqueous liquors were acidined with acetic acid, ether extracted, the extracts being washed with water, aried and the ether removed by 125 distillation. Postillation under reduced pressure yielded crude ethyl-a-formyl-B-

Byt. 110-135° C. ethylthio acrylate. at 7 mm. pressure.

C. PREPARATION OF a-(n-PEOPYL CAEB-OXY) MALONDIALDERYDE MONO ANTL. 13 parts of sodie ferregien-prepyl acetate were dissolved in 66 parts of water and added with stirring to a solution of 8 parts of aniline in a mixture of 43 parts of acetic acid and 186 parts of 10 water. The n-propyl-omilinomethylene acetate was precipitated as a slightly.

sticky yellow solid.

A suspension of 51 parts of the above n-propyl-anilinomethylene one ate in 100 15 parts of dry ether can 20 parts of ethyl formate was added in portions to 5 ports of sodium powder under 200 parts of dry ether. The mixture was refused for S hours and then poured ions water under 20 an atmosphere of COa. The other was then evaporated and the product filtered from the aqueous solution. If was a yellow solid, m.pt. 132°.

> D. PREPARATION OF G-CTARO-MALON-DIALDEHYDE MONO AMIL.

30 parts of sodio formyl acetonitrile were dissolved in 267 parts of water and added with stirring to a solution of 30 parts of aniline in a manure of 160 parts 30 of acetic acid and The parks of water. The anilinomethylene acetonerile was

precipitated slowly as a rellow sould.

M.pt. 119°.

A suspension of ? parts of the above 35 anilinomethylene sectionitrile, bu parts of dry ether and 4 pure of shall formate was added in portions to 11 parts of sodium powder under i(n) ports of dry ether. After complete addition the mix-40 ture was refluxed for 4 days and thea poured into water under an atmosphere

of CO2. The ether was evaporated and the product filtered as a you've solid. After crystallisation from ethyl alcohol 45 it melted at 183°.

The following Enamples stave to illus-

trate the invention ---

Example 3 BIS-2(3-EPHYL BENZOE, COOTES - 7 - CERB-ETHOXY PENTAMETRINE CYANTER TOTALE. Method (i). 10 parts of a carbethoxy malondialdehyde mone and, 30 parts of 2-methyl benzthinzole ethiodice and 200 parts of pyridine were refluxed together 55 for 3 minutes when the solution turned dark red. 6 parts of their thenine ware added with shaking and the solution allowed to cool before powering into water. The dyestuff crystallised, was filtered 60 and recrystallised from mental alcohol to give dark green crystals. M.pt. 230° with decomposition.

2 paris of stryl-a-Method (ii). tormyl-\$-ethylthic acrylate, 6 parts of 2methyl benzthiazole and 15 parts of 65 pyridine were heated together for 15 minutes, during which time a rich blue colour was formed. This solution was poured into water when the dyestuff crystallised as blue-green prystals. These 70 were well washed, dried and recrystallised from methyl alcohol. M.pt. 230° with decomposition.

This dyestuff, when incorporated in a gelatino silver bromide emulsion, im- 75 parts a band of sensitivity extending to 6800 A with a maximum at 6460 A.

#### EXAMPLE 2

BIS-2-(1-ETHYL QUINOLINE)-y-CARBETHOXY PENTAMETHINE CYANINE LODIDES.

10 parts of a-carbethoxy maloudiaidehyde mono anil, 30 parts of quivaldine ethiodide and 200 parts of pyridine were heated together for 3 minutes when the solution turned red-green. 6 parts of tri- 85 ethylamine were added and the solution refluxed for 30 minutes, during which time a green colour slowly appeared. The pyridine solution was poured into water when the dyestuff crystallisea. Recrystal- 90 lisation from methyl alcohol gave bluegreen crystals. M.pt. 253° (decomposi-

This dyestuff, when incorporated in a gelatino silver bromide emulsion. im- 90 parts a band of sensitivity outename to 7200 å with a maximum ar 690t å.

### EXAMPLE 3

BIS - 2 - (1.3.3-TRIMETHYL-INDOLENIEE)-Y-CARBETHONY PENTAMETHINE CHANINE 100

IODIDE. 10 parts of a-carbethoxy malandiaidehyde mono anil. 80 parts of 3:8:3-trimethyl indolenine methicaide and 200 parts of pyridine were reacted as my the 105 above Examples. The eyestaff was obtained as dark green-blue crystals upon dilution with water which, ween recrystallised from methyl alcohol, melted at 207° (decomposition).

### EXAMPLE 4

BIS - 2(3-8-ACETOXYETHYL BENZIHAZOLE)-Y -- CARBETHONY PENTAMETRINE CYANINE

10 parts of a-carbethoxy malondialde- 115 hyde mono anil. 31.6 parts of Craethyl benzthiazole \beta-hydroxv etaicdide and 100 parts of acetic anhydride were beated together for 2 minutes when the colour of the solution attained a deep red. The 120 solution was then cooled to 100°. 8 parts of triethylamine added with shaking, and the blue solution allowed to cook devely. The dyesruff was obtained by precipitation with other, washing with water and subsequent treatment with acetone. The dark blue solid obtained melted at 110°.

EXAMPLE 5

5 BIS-MAG-C-ACETOXYETHYL-5 - CHLOR-BENZ-SELAZOLE)-Y-CARBETHOXY PENTAMETHINE GYANISZ ADDIDE.

10 parts of a-carbethoxy malendialdehyde mone anil, 34 parts of 2-methyl-5-10 chler - benzitiazele-β-hydroxy ethiodide and 100 parts of acetic anhydride were heated together and treated as in the above Example. The dyestuff isolated as previously was obtained as dark green 15 powdery crystals. Li.pt. 154°.

EXAMPLE 6

RIS-2(3-3-ACETOXYETHYL BENZIHLAZOLE)-Y-TO TROPY CARDONY PENTAMETHINE OFAMINE LOBIDE.

diametry of a-n-propyl carboxy malendial diametry canachiazoie B-hydroxy ethiodide and 20 parts of a etic anhydride were heated together for 3 minutes. The solu-

25 then was then cooled to 100°, 1.5 parts of triothylamine added with shaking, and the time solution then cooled rapidly to room temperature. Excess ether was added to precipitate the dyestuff as a tar

which was washed with water and then treated with acctone to give the crystalline dressnit. This was recrystallised from methyl alcohol to give dark bluegreen crystals. Mint. 150° (decomposition).

gentino silver brownite emulsion, imparts a weak hand of sensitivity extending to 3330 A with a maximum at 6500 A.

40 Bramped 7

BIS- ONL O MUSCONTENINYL QUINOLINE)-y-n-FIM-PST, HARMONY PENTAMETITINE CYANINE 100FES.

45 malonalaldehyde mono anil. 3.1 parts of quantidine-F-rydresy ethiodide and 20 parts of social analydride were heated together and 1.5 parts of triethylamine added. The procedure was similar to that

of the provious Example. The dyestuff was amarined, after crystallisation from meant alcohol, as dark bine-green crystals. It the 124 (decomposition).

EXAMPLE S

BIS-2(3-ETHYL BENZTHIAZOLE) -  $\gamma$  - CYANO 55 PENTAMETHINE CYANINE IODIDE.

1.7 parts of a-cyano-malondialdehyde mono anil, 6 parts of 2-methyl benzthiazole ethiodide and 40 parts of acetic anhydride were neated together for 5 60 minutes, during which time the colour of the solution deepened to dark red. 1.6 parts of triethylamine were then added, and after another 3 minutes' refluxing, during which time a blue colour appeared, 65 the solution was cooled and the dyestuff filtered. When recrystallised from methyl alcohol it was obtained as dark brown crystals with a 4 rean reflex. M.pt. 268 (decomposition).

This divertuil, when incorporated in a gelatino silver promine emulsion, imparts a weak band of sensitivity extending to 6600 Å with a maximum at 6350 Å.

EXAMPLE 9
a.y-bis-3-(3-erhyl-2-thio-4-keto - tetra-

75

1.7 parts of a-cyano-malondialdehyde mono anil, 8.2 parts of N-ethyl rhodanic acid and 40 parts of acetic anhydride were 80 heated together for 5 minutes. 1.4 parts of triethylamine were then added and heating continued for 15 minutes, during which time the dye colour (dark greenblue) gradually appeared. The solution 85 was cooled and the dyestaff filtered. Recrystallisation from metyl alcohol gave blue crystals with a bright reflex. M.pt. 220° (decoraposition).

DE AMPLE 10.
BIS-2-(3-6 - ACETO EVENTE BENZTHIAZOLE)-

7-CYANG PENTAMETHINE GYANINE IODIDE.
1.7 parts of a-cyano malondialdehyde mono anil, 6.1% parts of 2-methyl benzthiazole-6-hydroxy ethiodide and 30 parts of acetic ambydrate were heated together for 5 minutes. I part of triethylamine added, and the solution refluxed for a further 3 minutes. The dyestuff was filtered, after cooling the solution, and 100 recrystoliased from methyl alcohol when it was obvained as dark blue crystals.
M.pt. 243' (decomposition).

Dated this 15% day of May, 1948. V. (ed.) LAFENT, Chartered, Patent Agent.

# COMPLETE SPECIFICATION

# Improvements the secretaring to the Production of Cyanine Dyestuffs and to the Sensitising of Photographic Emulsions

we, Ilford Limited a British Company, of 23, Roden Street. Uford, in the County of Essex, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production to of cyanine dyestuffs and preficultive to the production of symmetrical disarbocyanine dyestuffs courses by adestituting in the polymethine circle. It further relates to the sensitiving of the logical tenths.

15 emulsions.

According to the present invertion eyanine dyestuffs are prepared by condensing a compound of the general formula I:—

where R<sub>1</sub> is a nitrile (ON. in carbot rlic ester (COOR) group and R is a thiocher (—SR) or anil (2.7 f anom R living a hydrocarbon group, e.g. on all rlange of 1 to 4 carbon atoms or ar arrangement of 6 to 10 carbon atoms with a heterocyclic

We, Ilrord Limited a British Com- nitrogen compound containing a leactive on of 23 Roden Street. Uford, in the methylene group.

More particularly, according to this invention, the said heterocyclic compound 30 conforms to one or other of the following general formulæ II and III:—

$$N = (GH - GH)_{11} = G - GH_{3}$$

$$N = (GH - GH)_{21} = G - GH_{3}$$

$$N = (GH - GH)_{21} = G - GH_{3}$$

where R<sub>2</sub> is an alkyl, hydroxycleyl or 35 aralkyl group, Y<sub>1</sub> is an acid radic. a, D<sub>1</sub> is the residue of a five-membered or six-membered heterocyclic ring. n is nought or one, R<sub>3</sub> is a hydrogen atom or an alkyl, aralkyl or anyl group and D<sub>2</sub> is the residue 40 of a heterocyclic nitrogen-keto-methylene nucleus.

Accordingly as compounds of formulæ II or III are employed, so the products conform to formulæ IV or V:—

$$R_{2} = \frac{1}{2} - \frac{1}{2$$

The condensation more in effected in the presence of a base or in the presence of an acid anhydride legalities with a case. A base such as presented to us, a member of the contact the action of the contact the contact the contact the conjunction with a carbo which and early dride such as acetic anhydratic.

As already indicated R, may be a nitrile group or a an obligite easer group.

Examples of the letter are premis on the form —COOR where the an olkyt, e.g. of methyl, ethyl, planting of alkyl group, are a stormaring and pearlyl or naphthylmethyl, of an arrit group, e.g. phenyl or naphthylmethyl. It may be any of

the foregoing alkyl or aralkyl groups, or may be a hydroxyalkyl group sach as β-65 hydroxy ethyl or γ-hydroxy propyl. Where R<sub>2</sub> is an hydroxyalkyl group this will usually by acylated by the said condensing agent so that R<sub>2</sub> in the product will be an acyloxyalkyl group. R<sub>2</sub>, if not 70 a hydrogen atom, may be any of the foregoing alkyl, aralkyl or aryl groups.

Y, may be any acid radicis, for example halide (chloride, bromide, iodide), sulphate, sulphamate, perchlorate of p-75 toluene sulphanate.

D, may be the residue of any five-membered or six-membered heterocyclic ring systeminal uding this zoles and zoles, selenazolas and theirpolycyclic homologues such as this por the benzeve, naphthalene, acemachinene and anthrecene series; pyridino and the polycyclic homologues, such as quinciline and a and β-naphthoquinolines, lepiclines; indolenines; diazines such as pyrimidines and quinazolines; diazoles (e.g. thio-ββ¹-diazole); oxazolines, thiazolines and selenazolines. The polycyclic compounds of these series may be substituted in the carbocyclic rings with one or more groups such as alkyl, anyl, amino, hydroxy, alkoxy and methylene dioxy groups, or by halogen

15 atoms

1)2 may be the residue of rhodanic acid
(2-this - 4 - seto-tetrahydrothiazole), oxarhedanic acid (2-thio-4-keto-tetrahydrooxazole) and the N-1ydrocarbon substi20 miest deciratives of such compounds,
oxadoles, pyrazole-h-ones, hydantoin,
thio ayountoin, pseudohydantoin and

pseudorhich; denvoin.

The initial starting compounds of 25 general formula I may be prepared by reacting a compound of the formula CII, R. v.e. pretonitrise or an acetic ester, with a formic ester (preferably ethyl formally in the presence of powdered This yields the compound 30 sodram. R,-CH2-4-EC as its sodium salt. This product is they reacted with a mercaptan RSM s the presence of dry bydrochloric actor to is removed with aniline to produce 35 the thisatary or and of the formula is seached another with a formic ester (preferning edgy, formate) and powdered sodium to graid a product of the formula 40 L as required for use in the present

The resource is preterably effected using one molecular equivalent of the compound of frigular Levita substantially two molecular equivalents of the compound of formals II is all, by centing the reagents together, correctionly at the boiling point of the pass of said anhydride employed,

50 White the diestefts formed according to this invasion are sensitising dyes for allow action and sensitising dyes for allow action whategraphic emulsions.

The following illustrate the preparation of compounds of general formula 1:—

55 A. FOUNTABLEON OF C-CARBETHOXY MALON-

were dissolved in 100 parts of water and could with discharge a solution of 7 parts of of addition in a mixture of 40 parts of mode and 100 parts of water. The efficient little and place acctate was precipated as a decement yellow solid.

This preparation is analogous to that of 65 v. Pechmann, Berichte der Deutschen Chemischen Gesellschaft, 25, 1047.

A suspension of 30 parts of the above ethyl-anilinomethylene acetate in 100 parts of dry ether and 11.7 parts of ethyl 70 formate was added in portions to 3.62 parts of sodium powder under 200 parts of dry ether. A slight reaction ensued and afterwards the solution was refluxed for 8 hours and then poured into water 75 under an atmosphere of CO2. The water was ether extracted, the extracts dried over sodium suiphate and the ether removed by distillation. The product was distilled under reduced pressure, b.pt. 80 197° at 8 mm. pressure to give an oil which solidified on cooling to a yellow crystalline mass.

B. Prefaration of Ethyl-α-formyl-β-ETHYLPHIO ACRYLATE.

14 parts of sodio formyl ethyl acetate and 25 parts of ethyl mercaptan were mixed together with 25 parts of dry ether, and dry HCl gas passed through the mixture for 2 hours with cooling. 90 After being allowed to stand overnight, the solution was poured into dilute sodium carbonate solution, ether extracted, aried over sodium sulphate anhydrous, and the ether evaporated. 95 Distillation under reduced pressure yielded β-ethylthio ethyl acrylate. B.pt. 160—165° at 30 mm, pressure.

Il parts of the above β-ethylthioethyl acrylate and 6 parts of ethyl formate 100 were mixed with a little dry ether and reacted with 1.5 parts of sodium powder also under dry ether. After addition the mixture was heated for 24 hours and poured into water under an atmosphere 105 of earbon dioxide. The aqueous liquors were acidified with acetic acid, ether extracted, the extracts being washed with water, dried and the ether removed by distillation. Discillation under reduced 110 pressure yielded grade ethyl-a-formyl-β-ethylthio acrylate. B.pt. 110—135° C. at 7 mm. pressure.

C. PREPARATION OF a (n-PROPYL CARB-ONY) MALONDIALDEHYDE MONO ANIL. 115
13 parts of sodio formyl-n-propyl acetate were dissolved in 66 parts of water and added with stirring to a solution of 8 parts of aniline in a mixture of 43 parts of acetar acid and 186 parts of 120 water. The n-propyl-anilinemethylene acetate was precipitated as a slightly sticky vellow solid.

A suspension of 51 parts of the above n-propyl-pullinomethylene acetate in 100 125 parts of dry erher and 20 parts of ethyl formate was added in portions to 5 parts

of sodium powder under MCO parts of dry ether. The mixture was stirred for 8 hours and then pourse into water under an atmosphere of Co. The ether was 5 then evaporated and the product filtered from the aqueous solution. It was a yellow solid, m.pt. 132°.

### D. PREPARATION OF A CVASO-BLALOW-DIALDEHYDE MONO ANTO

30 parts of socio formayl acefonitrile were dissolved in 267 parts or water and added with stirring to a sciution of 30 parts of aniline in a mixture of 160 parts of acetic acid and Tail parts of water. 15 The anilinomethylene acetro arile was precipitated slowly as a princip solid. M.pt. 119°.

A suspension of I parts of the above anilinomethylene acaremitate, 60 parts 20 of dry ether and 4 (a) is of other formate was added in portions to Li parts of sodium powder under 100 parts of dry ether. After complete addition the maxture was refluxed for a days and then 25 poured into water and a amosphere of CO2. The other was emphysical and the product filtered as a parlow solid After crystallisation from sibel alcohol it melted at 183°.

The following Examples served to Misstrate the invention: -

#### Example 1

BIS-2(3-ETHYL BENEGOTS ACCED - Y - CACB-ETHOXY PENTAMETERS OF A TITE TODILE. 35 Method (i). 10 mars of an arbethoxy malondialdehyde work out, for parts of 2-methyl benzthiazole estimate a and 200 parts of pyridine were astressed ingether for 3 minutes when the solution turned

40 dark red. 6 parts of triedly a line were added with shaking and the solution allowed to cool before possing note water. The dyestuff erystallised, were filtered and recrystallised from more of alsohol 45 to give dark green reparals. M. ot. 230°

with decomposition. tarts of ethyl-a-Méthod (ii). formyl-B-ethylthic and have. I make on Cmethyl benzthiazoro and to parts of 50 pyridine were Leaben bayesher for 15 minutes, during which have a wich blue colour was formal. This column was poured into water when the dynamif crystallised as blue-green arrestals. These

55 were well washed, dried as a recervisial. lised from methyl alothol 35 pt. 200 with decomposition.

This dyestuff, when are more weed in a gelatino silver bromme enterson. mi-60 parts a band of sensitivity extending to 6800 A with a maximum of 6400 A.

### EXAMPLE 2

BIS-2-(1-ETHYL QUINOLINE)-Y-CARSETHOXY PENTAMETHINE CYANINE TODIDE.

10 parts of a-carbethoxy malandialde- 65 hyde mono anil, 30 parts of quinaddine ethiodide and 200 parts of pyridine were heated together for 3 minutes when the solution turned red-green. 6 parts of triethylamine were added and the solution 70 refluxed for 30 minutes, during which time a green colour slowly appeared. The pyridine solution was poured into water when the dyestuff crystallised. Recrystallisation from methyl alcohol gave ofue- 75 green crystals. M.pt. 252° (decomposition).

This dyestuff, when incorporated in a gelatino silver bromide emulsion, umparts a band of sensitivity extending to 80 7200 A with a maximum at 6900 A.

### EXAMPLE 3

BIS - 2 - (1.3.3-TRIMETHYL-INDOLEMENE)-Y-CARBETHOXY PENCAMETHINE CYANINE

10 parts of a-carbethoxy maloudialdehyde mono anil, 30 parts of 2:3:3-trimethyl indolenine methiodide and 200 parts of pyridine were reacted as ir the above Examples. The dyestriff was ob- 90 tained as dark green-blue crystals upon dilution with water which, when recrystallised from methyl alcohol, meited at 207° (decomposition).

### 95 EXAMPLE 4

BIS - 2(3-β-ACETOXYWTHYL BENZTHIAZCLE)-Y-CARBETHONY PENTAMETHINE CHINENE

10 parts of a-carbethoxy maloudialdehyde mono anil, 31.6 parts of 2-methyl 100 benzthiazole β-hydroxy ethicdide and 100 parts of acetic anbydride were heated together for 2 minutes when the colour of the solution attained a drep red. The solution was then cooled to 100°. C parts 105 of triethylamine added with shaking, and the blue solution allowed to coch slevely. The dyestuff was obtained by macipitation with ether, washing with water and subsequent treatment with acetone. The 110. dark blue solid obtained melted as 110°.

### Example 5 BIS-2(3-B-ACETOXYFTHYL-5 - THIGH-BINIZ-THIAZOLE)-Y-CARBECHOXY PENTAMETHINE CYANINE IODIDE.

10 parts of a-carbethexy malouchaldebyde mono anil, 34 parts of 2-methyl-5chlor - terzshiazole-G-hydrovy ethiodide and 100 parts of acetic many drum were heated together and treated as in the 120 above example. The dyesnut is laud as previously was obtained as dayl green powdery crystals. M.pt. 154°.

EXAMPLE 6

615-1 (B-B-AD CONVETTIVE BENZTHIAZOLE)-Y(B-PEGPY. - CARRONY) PENTAMETHINE
CYLLEINE ICHAE.

5 2.30 parts of z-n-propyl carboxy malon-dialdehyde mono anil, 3.1 parts of 2-methyl berzihiazole-3-hydroxy ethiodide and 30 parts of acetic anhydride were heated together for 3 minutes. The solution was then cooled to 100°, 1.5 parts of triothylamine added with shaking, and the like solution then cooled rapidly to

added to precipitate the dyestuff as a tar which was washed with water and then treated with acctone to give the crystalline assembly alcohol to give dark bluegreen crystals. M.pt. 150° (decomposition)

gentrio silver bromide emulsion, imparts a weak land of sensitivity extending to 6500 \$\delta\$ with a maximum at 6500 \$\delta\$.

25

PIS-2-4 (-4.0) ONTEVILL QUINDLINE)-y-(nPROPYL: ARBONY) PENTAMETHINE CTANINE
LONGO.

30 major diableareds mose anil, 3.1 parts of quincildires. Aydroxy ethiodide and 20 parts of analydride were heated together and 15 parts of triethylamine adder. The procedure was similar to that

35 of the previous example. The dyestuff was codamed, after crystallisation from metays actual, as dark blue-green crystain. In pt. 124° (decomposition).

\*\*Example 8

40 bis-2(0-minute benezhiazole) - y - cyano pennangan de cyanene iodide.

more anil, it parts of 2-methyl benzthian, a claimede and 40 parts of acetic 45 ampaired were assed together for 5 process of any which time the colour of the soil our deepened to dark red. 1.6 parts of cristivianine were then added, and after marker 3 minutes' refluxing.

the relation was decided and the dyestuff name. When recrystallised from methyl archief with a preen reflex. M.pt. 268° 55 (dec myorizon).

gelation across brownine emulsion, imparts a work band of sensitivity extending to their a parts and a parts of the continuum of 6350 Å.

6) EMAIRIE 9

a.y - mea-field office of the to-4-keyo - thera
to measurement of the following propers.

parts of N-ethyl rhodanic so act with the parts of N-ethyl rhodanic

heated together for 5 minutes. 1.4 parts of triethylamine were then added and heating continue I for 15 minutes, during which time the dye colour (dark greenblue) gradually appeared. The solution 70 was cooled and the dyestuff filtered. Recrystallisation from metyl alcohol gave blue crystals with a bright reflex. M.pt. 220° (decomposition).

EXAMPLE 10. 75

BIS-2-(3-\$\beta\$ - ACETOMYETHYL BENZTHLAZOLE)
\[
\gamma-CYANO PENTAMUTHINE CYANINE IODIDE.

1.7 parts of a-cyano malondialdehyde

mono anil, 6.12 parts of 2-methyl benzthiozole-\$\beta\$-hydromy ethiodide and 30 parts

of acetic anhydride were heated together

for 5 minutes, 1 part of triethylamine

added, and the solution refluxed for a
further 2 minutes. The dyestuff was
filtered, after cooling the solution, and
recrystallised from methyl alcohol when

it was obtained as dark blue crystals.

M.pt. 243" (decomposition).

EXAMPLE 11
BIS-2-(3-ETHYL BENZSELENAZOLE) -  $\gamma$  - CARB- 90

19.6 parts of 2-methyl benzselenazole and 18.6 parts of methyl-p-toluene sulphonate were fused at 100° C. for 3 hours, 10 parts of z-carbethoxy malondialdehyde 95 mono anil and 200 parts of acetic anhydride were added, and the mixture boiled for 30 minutes. Pacess triethylamine was then added with cooling, whereupon the dyestuff was formed and precipitated from 100 the blue solution as a tar. This on treatment with acetone gave green crystals of the dyestuff, m.pr. 150° C. (with decomposition).

Having now paraceularly described and 105

ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the preparation of 110

eyanine drestoffs which comprises condensing a compound of the general formula:—

where R, is a nitrile (CN) or carboxylic 115 ester (COOR) graded X is a thioether (SR) or and (NHR) group, R being a hydrocarbon group, with a heterocyclic nitrogen compound containing a reactive mathylene group.

2. Precess for eding to claim 1 wherein the horses while compound containing a reactive methy one group is a compound of the general formula:—

where R is alkyl, available or legitousy-alkyl, Y, is an acid and tale. It is a residue of a five-membered or a x-monal area ring and n is nought or one.

3. Process according to their 1 or 2 wherein the reaction is offected by heating the reagents in the presence of a base.

4. Process according to pay a site process according to pay a site process of a careovery and a strong base.

5. Process according to rain a where-15 in the anhydride englored is motic anhydride and the base in whether mine.

6. Process according to any or claims 2 to 5 wherein the residue line as indolerance of a benzthiazole, quit line as indolerance maleurs.

in the heterocyclic control of containing a reactive methylens group as a reactive for the general formula —

wherein R<sub>a</sub> is a house of a rm or an alkyl, aralkyl or any state and R<sub>a</sub> is the residue of a house particle nitrogen-keto-methylene ring.

30 S. Process according to the warms in the residue La to the mount of a rhodanic acid unity.

9. Process for the production of a cyanine dyestuff substantially as senforth in any one of the foregoing specific 35 Examples 1 to 11.

10. Cyanine dyestuffs wherever prepared or produced by any of the processes hereinbefore described and claimed.

11. A photographic emulsion contain- 40 ing in sensitising amount a dyestuff of the general formula:—

where R<sub>1</sub> is a nitrile or carboxylic ester group, R<sub>2</sub> is an alkyl, aralkyl, hydroxy- 45 alkyl or acyloxyalkyl group. F<sub>1</sub> is an acid radicle, D<sub>1</sub> is a residue of a five-membered or six-membered ring, and n is nought or

12. A photographic emulsion contain- 50 ing in sensitising amount a dyssbuff of the general formula:—

$$R = 0 - 0 = 0 = 0 = 0 = 0 = 0 = 0 = 0$$
 $R = 0 = 0 = 0 = 0 = 0$ 
 $R = 0 = 0 = 0$ 

where  $R_1$  is a nitrile or caronylic ester group,  $R_2$  is a hydrogen arom or an advel, 55 aryloc aralkyl group, and  $R_2$  is the residue of a heterocyclic nitrogen-keto-mothylene ring.

Dated this 6th day of May, 1949

V. GALLAFENI, Chartered Fateni Agant.

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